Surfactant-Enhanced Aquifer Remediation (SEAR) for DNAPL Removal

Naval Facilities Engineering Service Center

Duke Engineering & Services

I. Characterization of DNAPL Zones

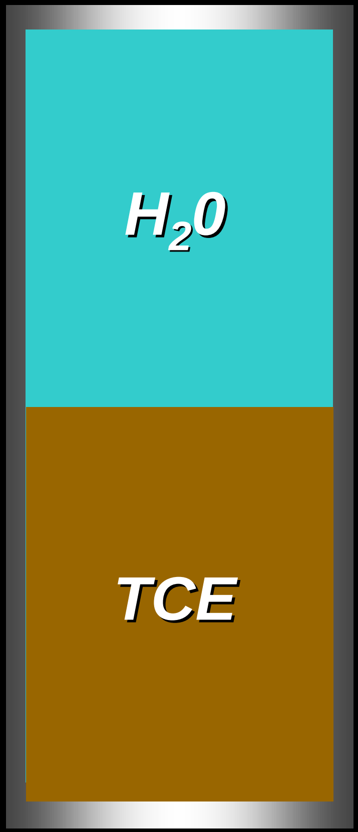
II. Surfactant-Enhanced Aquifer Remediation (SEAR)

Presentation Overview:
I. Characterization of DNAPL Zones

- **Introduction**
- Conventional methods
  - locating DNAPL
  - measuring DNAPL
  - NAPL algorithm
- Partitioning interwell tracer test (PITT)
  - Principles
  - Applicability
  - Design and Implementation
- Characterization examples

What is DNAPL?

DNAPL or dense, nonaqueous-phase liquid refers to an organic liquid, such as a chlorinated solvent, which has a density greater than water.



DNAPL Properties: Some values

DNAPL	Density (g/mL)	Solubility (mg/L)	Viscosity (cP)
Trichloroethylene (TCE)	1.46	1400	0.57
Perchloroethylene (PCE)	1.63	240	0.90
1,1,1-Trichloroethane (TCA)	1.33	1250	0.84
Coal tar	1.02	---	10-100 depends on weathering

Water has a density of 1 g/mL and viscosity of 1 cP.

Forms of DNAPL

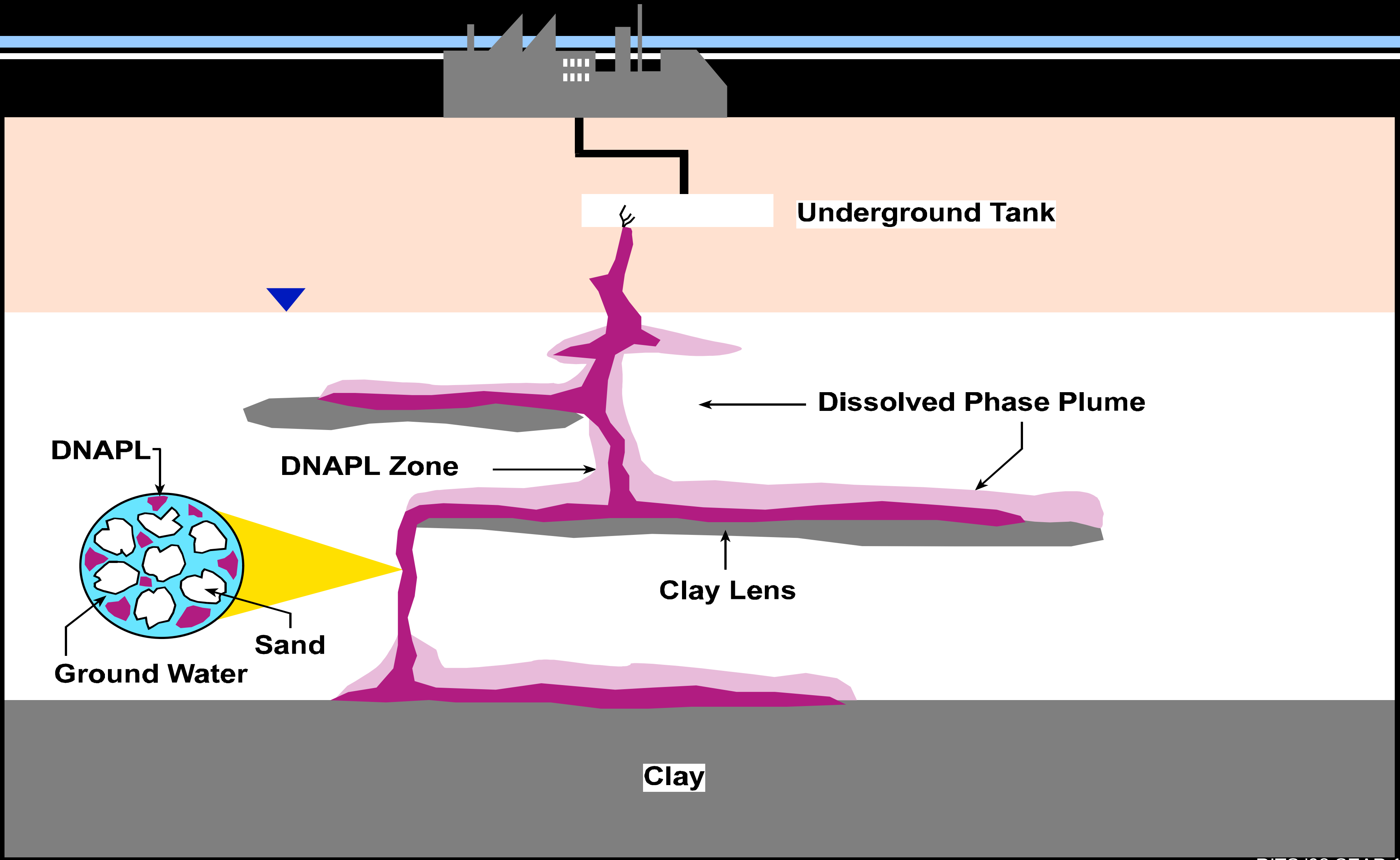
In the subsurface, DNAPL can be found in two forms:

- Free-phase DNAPL or mobile DNAPL which is under positive pressure and will drain to a well or a trench;
- Residual DNAPL which is held ("trapped") under capillary pressure by the surfaces of the aquifer containing the DNAPL.

The DNAPL Problem

- Small volumes of spilled DNAPL produce huge plumes.
- Most DNAPLs have low aqueous solubilities and are slowly biodegraded; thus they are very slowly removed by conventional pump and treat or natural processes.
- Because DNAPL is denser than water, it sinks until it reaches an impermeable layer. Because this can be several hundred feet below ground surface, DNAPL can be very difficult to locate and measure.

Schematic of DNAPL in the Subsurface



An example DNAPL contamination problem

- Consider one cubic meter of sand aquifer:
- porosity = 0.30, therefore 1 pore volume contains 300 L of groundwater;
- if residual DNAPL saturation = 0.10, 1 pore volume contains:
  - 270 L of groundwater and
  - 30 L of DNAPL

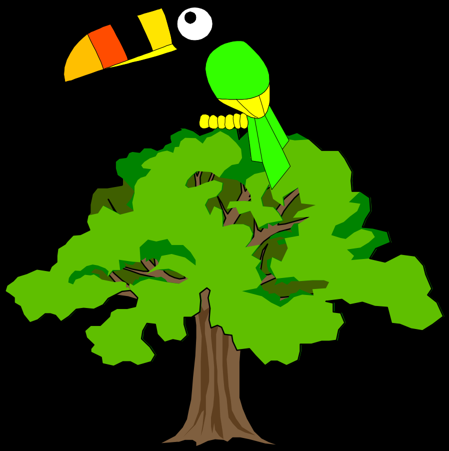
An example DNAPL contamination problem (cont.)

The mass of DNAPL is distributed as follows:

- assume DNAPL is TCE which dissolves to its aqueous solubility of 1400 mg/L;
- this means that the cubic meter of sandy aquifer contains 270 L x 1.4 g/L or ~ 400 g = 0.4 kg of dissolved TCE (at saturation)
- but amount of TCE DNAPL is 30 L x 1.46 kg/L = 44 kg (100 times the dissolved mass!)

Purpose of DNAPL characterization

- To locate the DNAPL
  - identify permeable and less permeable zones
  - define contour of confining layers
- To estimate the quantity of DNAPL present
  - Is there free-phase DNAPL?
  - What is the saturation of residual DNAPL?



The necessity of conventional methods

- Geophysical techniques such as seismic reflection have yet to be validated for DNAPL detection.
- Continuous cored soil samples can help identify potential migration pathways for DNAPL.
- Contaminant concentrations from soil and groundwater samples are necessary for remedial design and are the default for regulatory decisions.

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Common bloopers in locating DNAPL with conventional methods

- Sample preservation not used
  - coring of VOC-contaminated sediments without preservation will result in significant losses of VOCs and the possible identification of false negatives
- Missing or incomplete boring logs
  - complete lithologic data are needed to determine migration pathways for DNAPL
- Wells not screened into the aquifer-aquitard interface
  - free-phase DNAPL will tend to sink until it reaches a zone of lower permeability; thus a monitoring well screened in the middle of a permeable zone is not likely to yield DNAPL

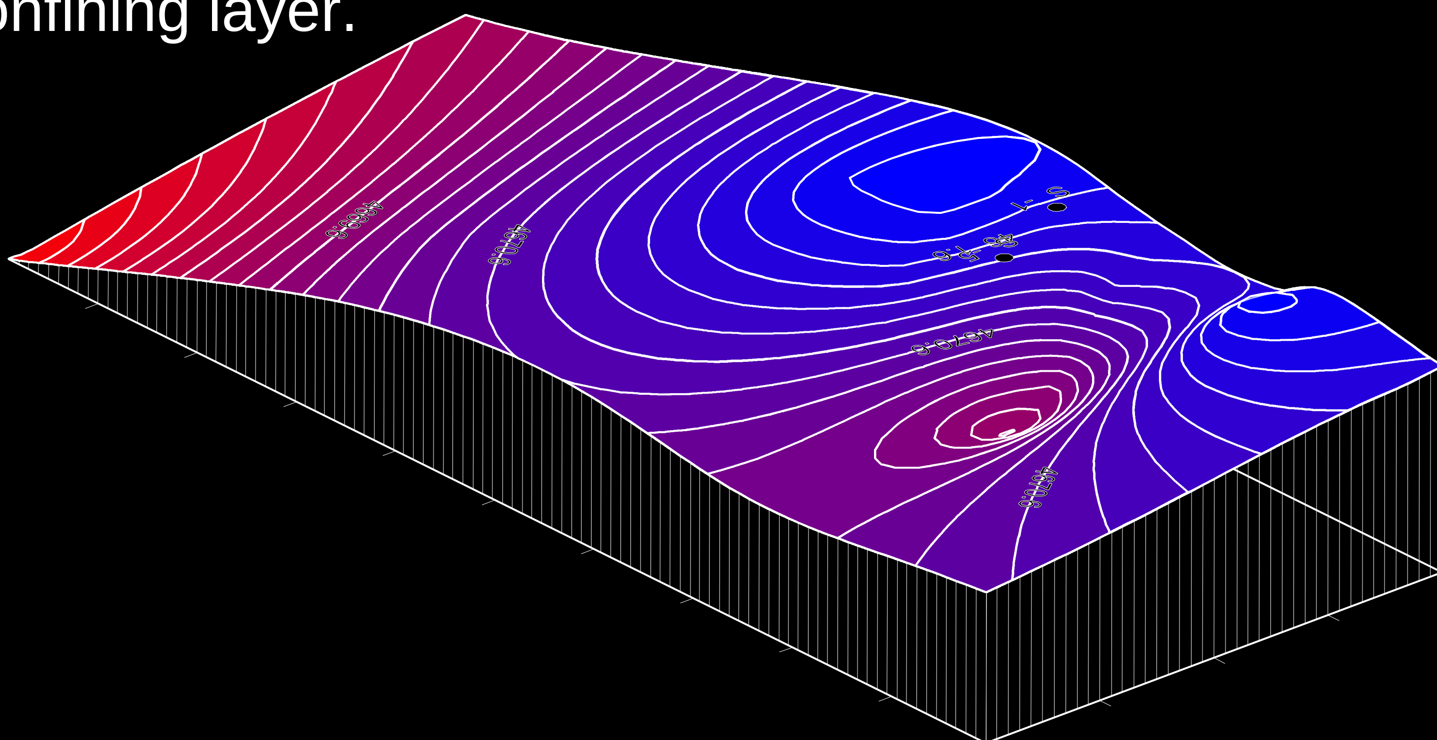
Conventional Methods: locating DNAPL

1. Perform soil sampling of suspected source areas using methanol as a preservative
   - perform continuous coring; direct push technology, i.e. Geoprobe, is cheapest, and allows discrete water samples to be collected
   - use sample tube liners to minimize VOC losses;
   - a photoionization detector (PID) is used to select ‘hot’ portions of the soil core for sampling & preservation

2. If wells are being installed in the source area for the collection of groundwater samples:
   - Install into the aquitard/aquifer interface and use stainless steel screen.
   - Avoid smearing of clays from the vadose zone or upper portions of the aquifer.

Conventional Methods: locating DNAPL

3. Mapping the depth to the confining layer (obtained from CPT data or boring/well logs) to obtain a contour of the surface is useful because DNAPL tends to pool in the depressions of the confining layer.



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Conventional Methods: Measuring DNAPL Saturation

1. Collect the soil sample with preservation.

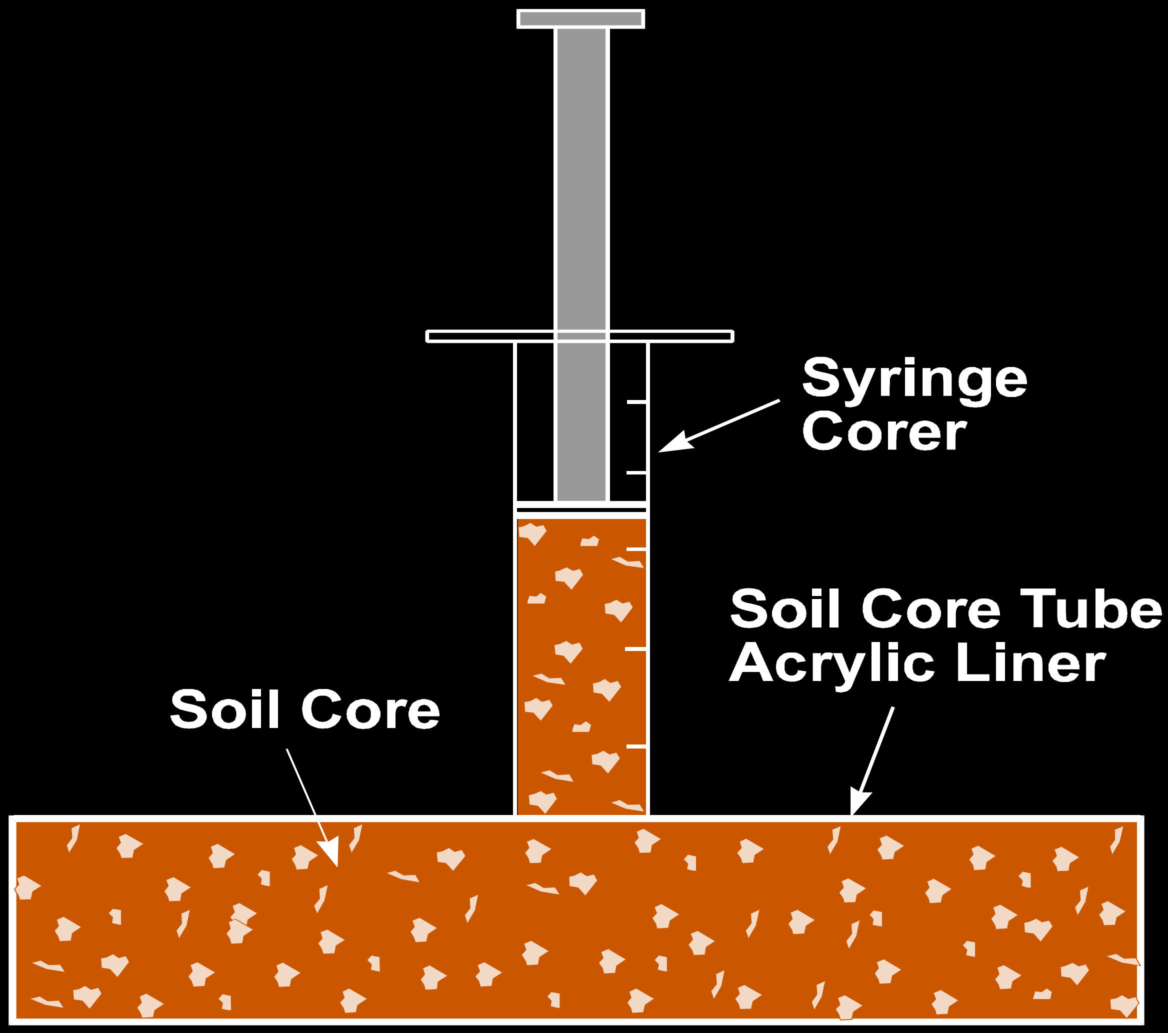
2. Analyze the extract (preservative) for DNAPL and backcalculate soil concentrations.

3. Use soil concentrations to determine the residual DNAPL saturation in the soil.

Conventional Methods: Measuring DNAPL Saturation

1. To collect the soil sample with preservation in the field:
   - weigh 40-mL vial with 15 g methanol;
   - collect soil core, subdivide;
   - add 20 to 30 g sediment using a syringe corer;
   - add sufficient methanol to submerge sediment,
   - reweigh the vial, agitate the sample, cool on ice

A syringe corer



Conventional Methods: Measuring DNAPL Saturation (cont.)

2. To analyze the methanol extract:
   - Dilute extract (minimum 10-fold dilution)
   - Use GC for analysis
   - Backcalculate soil concentrations

Conventional Methods: Measuring DNAPL Saturation (cont.)

3. Based on:

- soil concentrations,
- estimates of the soil porosity,
- soil organic content (FOC),
- and moisture content
  (=soil porosity for an aquifer sample),

the residual DNAPL saturation in the soil can be calculated using an algorithm such as NAPLANAL.

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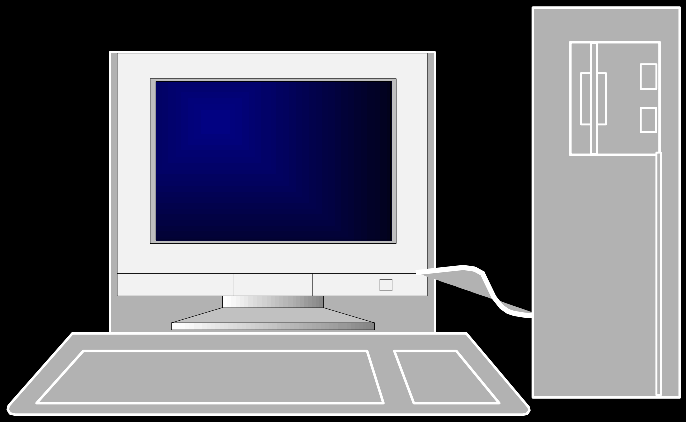
THE NAPLANAL ALGORITHM

- If DNAPL exists in a water-saturated core, the DNAPL components are partitioned among three phases:
  - soil or rock surface
  - water
  - DNAPL
- *NAPLANAL* assumes equilibrium partitioning between these phases.

THE NAPLANAL ALGORITHM (cont.)

- For additional information on NAPLANAL, see Spring ‘97 issue, *Ground Water Monitoring & Remediation*
- *NAPLANAL* will soon be downloadable from the web!



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Partitioning Interwell Tracer Tests (PITTs)

The weakness of using soil cores to find DNAPL is that, in heterogeneous soils, it is easy to miss DNAPL.

An alternative is to sweep the suspected zone of contamination with conservative and partitioning tracers in a partitioning interwell tracer test (PITT).
A PITT can:

- detect
- quantify
- and determine in an interwell space the spatial distribution of NAPL.

Partitioning Interwell Tracer Tests (PITTs), cont.

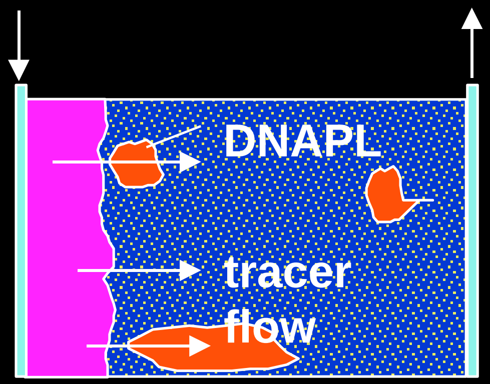
- Developed for DNAPL site characterization by Gary Pope at UT Austin.
- Adopted by EPA & SERDP for performance assessment of innovative remedial technologies at Hill AFB, Utah, by university consortium.
- Over 30 conducted since 1994.

Partitioning Interwell Tracer Tests (PITTs)

- Residual DNAPL saturation is estimated by comparing the retardation of tracers which partition into the DNAPL phase, e.g. alcohols, to tracers which are not retarded, e.g. bromide.
- Provides useful data for designing and assessing the performance of DNAPL remediation technologies.

Partition coefficients

$$\text{Partition coeff.: } K = \frac{\text{Conc. of tracer in DNAPL}}{\text{Conc. of tracer in water}}$$



So, the larger K is, the more the tracer partitions into the DNAPL and the more it becomes retarded by the presence of DNAPL.

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PITTs: Applicability

- Can be performed in any formation with reasonable permeability ($\geq$ 0.0005 cm/sec)
  - vadose zone (with gas tracers)
  - saturated zone
  - fractured bedrock
- Not amenable to highly heterogeneous subsurfaces

PITTs: Advantages/Disadvantages

- Advantages
  - Can estimate DNAPL saturation over a large volume compared to soil cores; therefore maximizes your chances of finding DNAPL.
  - The method is very sensitive and can measure down to <3% residual DNAPL saturation.
- Disadvantages
  - Not economical for sites with low permeability (<0.0005 cm/sec).
  - The presence of natural organic carbon may cause some difficulty with the interpretation of the results.

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Protocol for PITT Design & Implementation

1) Characterize DNAPL zone

2) Select tracers

3) Develop geosystems model of the aquifer and run simulations to complete the final design

4) Conduct conservative tracer test for further refinement of flowrates (optional)

5) Conduct PITT

6) Data analysis

Characterize DNAPL zone

- Collect soil cores from the zone of suspected DNAPL contamination.
  - Core analysis
    - What is the organic carbon content?
    - What is the grain-size distribution?
    - What is the vertical DNAPL distribution?
    - What is the DNAPL composition?
  - Collect material for tracer selection
- Install well array
  - hydraulic testing
    - What is the permeability of the aquifer?
    - What are the maximum pumping rates?
    - Where are the hydraulic boundaries?
  - free-phase DNAPL removal (if present)

Protocol for PITT Design & Implementation

1) Characterize DNAPL zone
2) **Select tracers**
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6) Data analysis

Tracer selection

- Liquid phase experiments
  - Measure the static partition coefficients of various tracers with site DNAPL
  - Select tracers with suitable range of partition coefficients for the DNAPL
- Soil column experiments
  - Determine whether the uncontaminated soil causes retardation of the tracers
  - Validate static partition coefficient measurements

Tracer Selection Criteria

- Suitable partition coefficients
- Insensitivity to the precise NAPL composition
- Low adsorption
- Environmental acceptability
- Chemical and biological stability
- Good availability
- Inexpensive
- Low detection limit

Some common tracers and relative costs

Tracer	Partitioning behavior	Cost/kg
Potassium Bromide	Conservative	$58.50
Methanol	Conservative	$5.70
1-Propanol	Conservative	$2.26
4-methyl-2-pentanol	Partitioning	$17.50
1-Hexanol	Partitioning	$2.72
2-ethyl-1-hexanol	Partitioning	$13.16
1-Heptanol	Partitioning	$29.12
1-Octanol	Partitioning	$4.81

Protocol for PITT Design & Implementation

1) Characterize DNAPL zone
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5) Conduct PITT
6) Data analysis

Pre-PITT Conservative tracer test

- Recommended if significant subsurface heterogeneity is suspected
- Measure sustainable injection and extraction rates at each well
- Identify lower permeable zones and adjust injection and extraction rates accordingly

Protocol for PITT Design & Implementation

1) Characterize DNAPL zone
2) Select tracers
3) Develop geosystems model of the aquifer and run simulations to complete the final design
4) Conduct conservative tracer test for further refinement of flowrates (optional)
5) **Conduct PITT**
6) Data analysis

Conduct PITT

- Mix tracers and sample to confirm composition
- Inject ~0.5 pore volumes (PV) of each tracer
- Follow with 5 PV of water
- Collect samples at extraction wells
  - first PV, 20-25 samples/well
  - second PV, 12-15 samples/well
  - third PV to the end, 5-8 samples/well

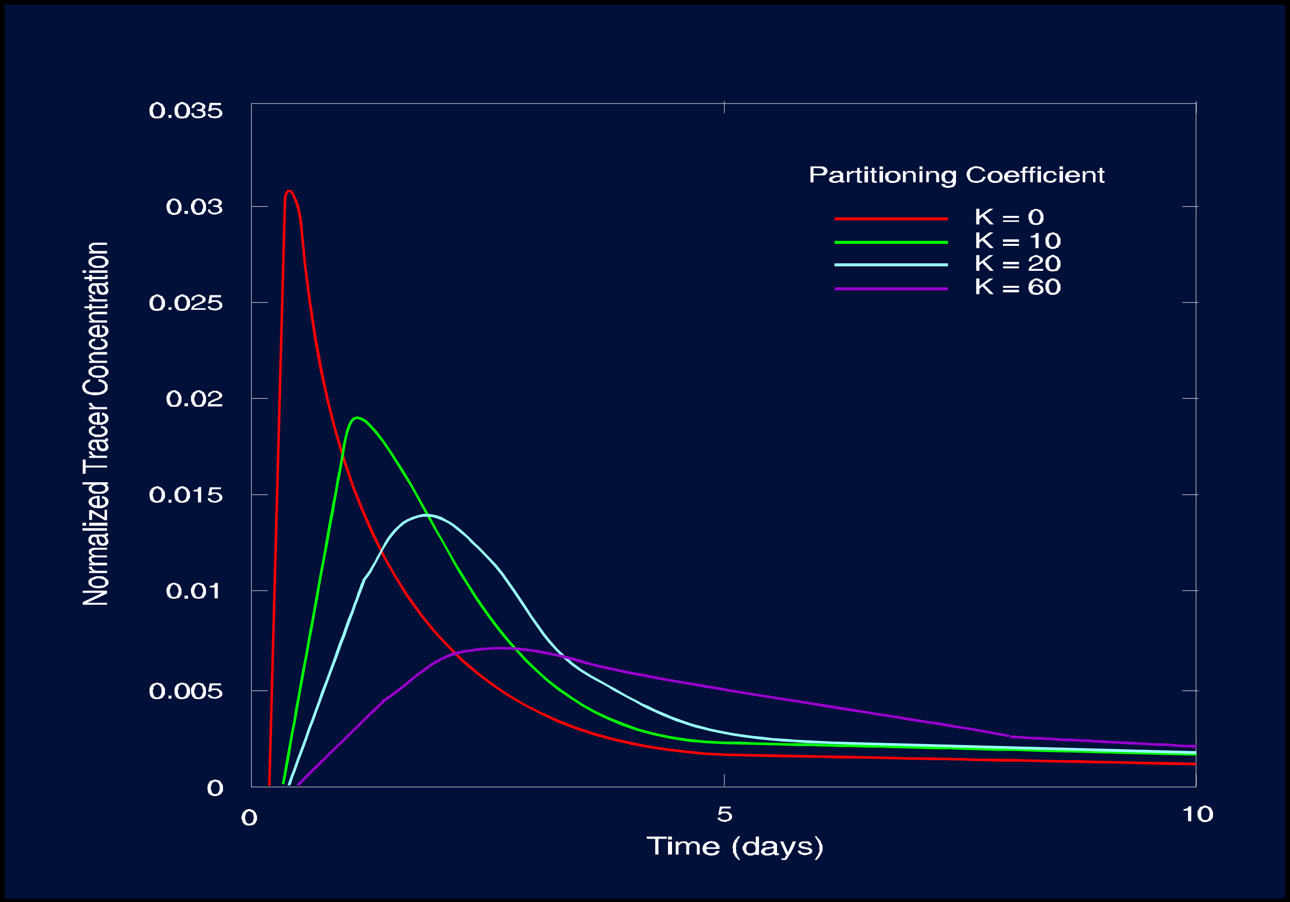
Protocol for PITT Design & Implementation

1) Characterize DNAPL zone
2) Select tracers
3) Develop geosystems model of the aquifer and run simulations to complete the final design
4) Conduct conservative tracer test for further refinement of flowrates (optional)
5) Conduct PITT
6) **Data analysis**

Data analysis

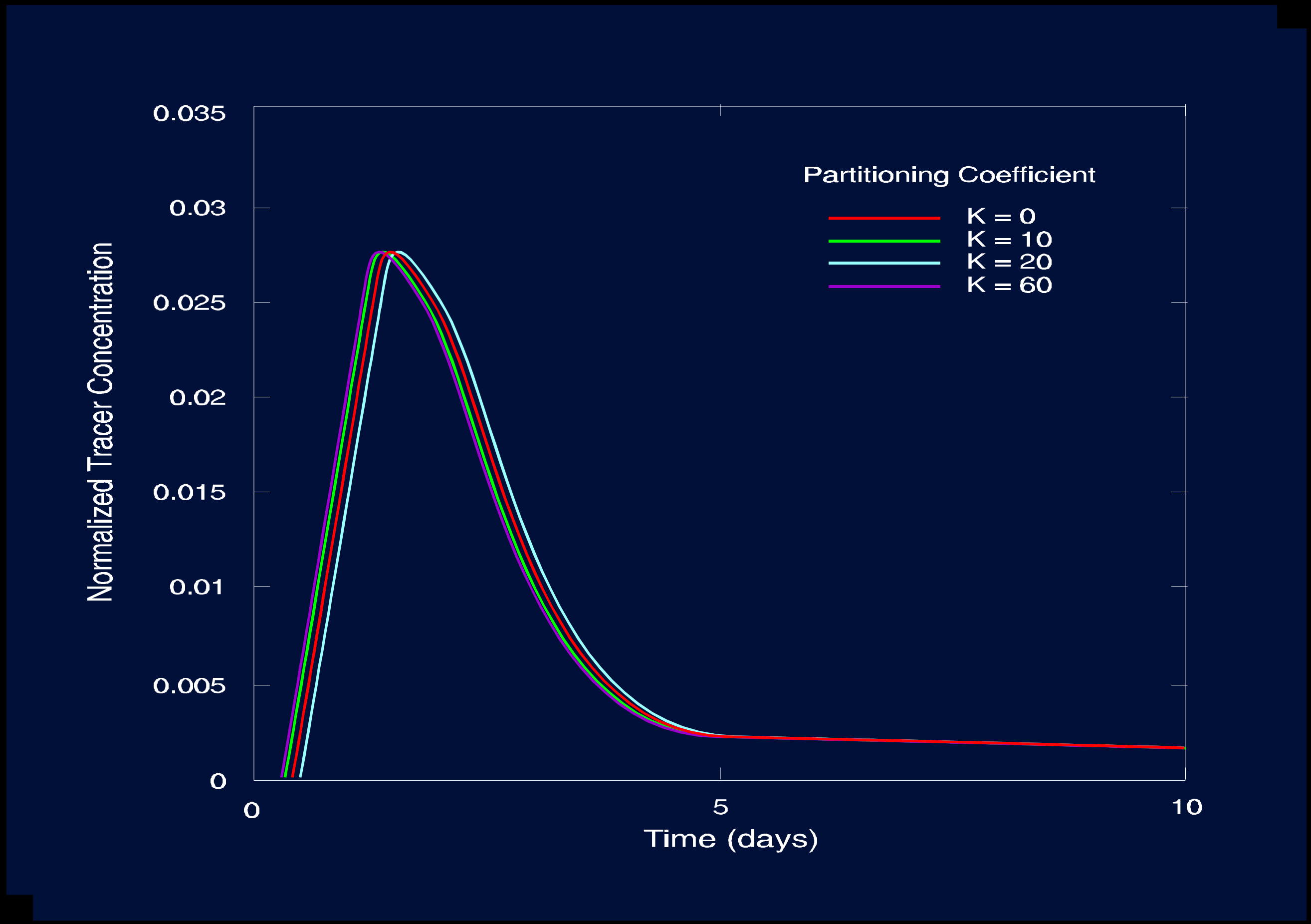
- Compare the maximum peak in the breakthrough curves. A peak separation can usually be observed for ≥ 10% residual DNAPL saturation.
- For lower saturations, the tails (curves which follow the peak) are compared. A separation of tails indicates the presence of residual DNAPL.

PITT: Tracer concentration curves



Tracer concentration curves when NAPL is encountered in the test zone

PITT: Tracer concentration curves



Tracer concentration curves after NAPL has been successfully remediated

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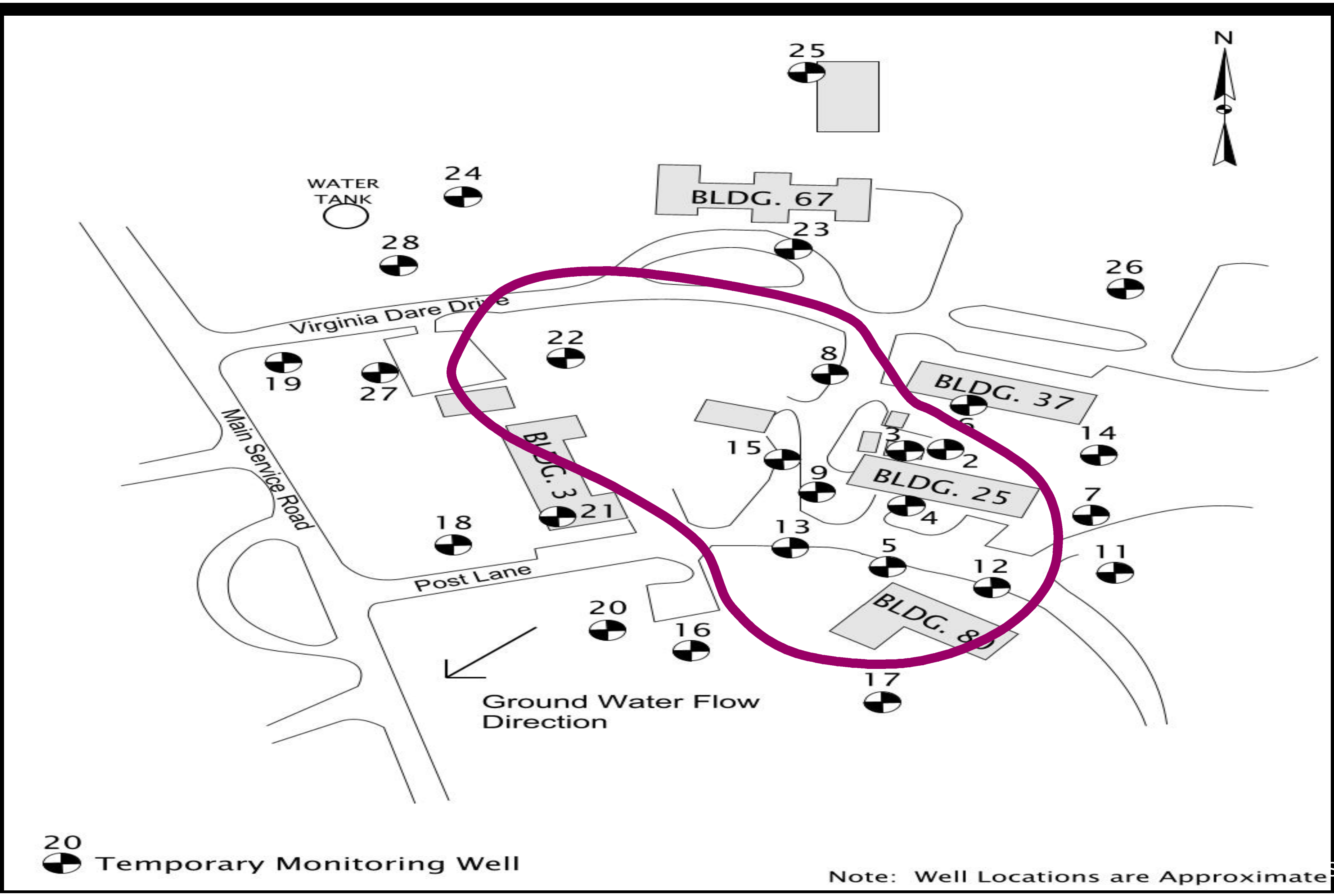
Characterization example: Site 88, Dry Cleaning Facility, MCB Camp Lejeune, NC

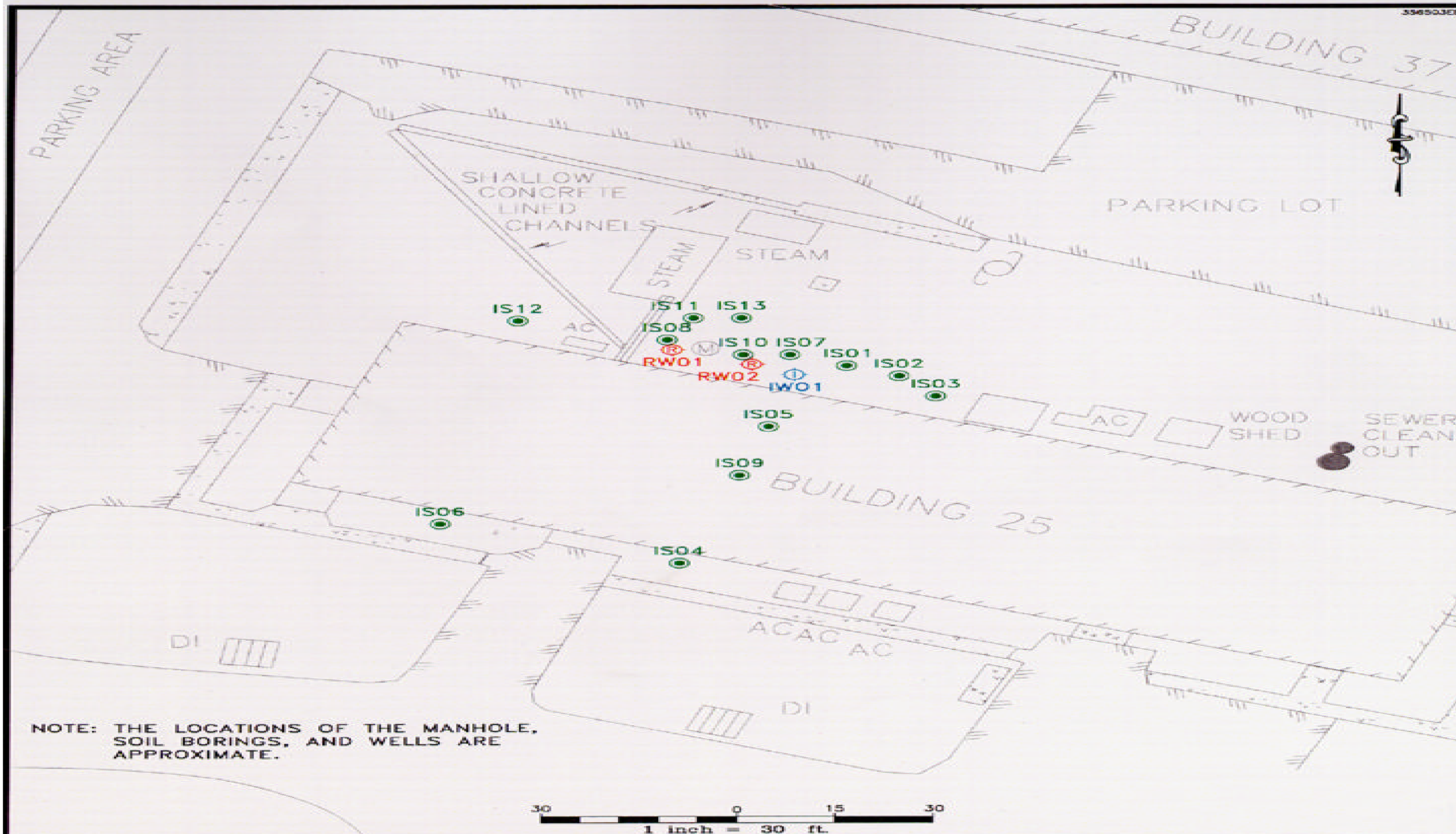
Primary GW contaminant: PCE (still in use as a dry-cleaning solvent)

Site 88, MCB Camp Lejeune, NC



Existing data

- GW sampling data showed the highest PCE concentrations at Temporary Well (TW) 3 (14 mg/L), TW-4 (33 mg/L) and TW-8 (54 mg/L).
- These wells are screened between 5 and 15 ft and other boring logs show that a confining layer begins at 17 ft.
- Where and at what depth should you look for DNAPL?



LEGEND

IS12 — SOIL BORING

RW01 — RECOVERY WELL

IW01 — INJECTION WELL

— MANHOLE

FIGURE 1
SOIL BORING AND WELL LOCATION MAP
OPERABLE UNIT NO.15 (SITE 88)
DNAPL INVESTIGATION

MCB, CAMP LEJEUNE, NORTH CAROLINA

Phase 1 DNAPL investigation: soil sampling

Using a Geoprobe rig and methanol preservation, samples were collected from
11 continuously cored borings at the site.
The highest PCE hits were detected in the following borings:

- IS08 (17.5 ft, 9,500 mg/kg),
- IS10 (17.2 ft, 19,000 mg/kg),
- and IS11 (16.4 ft, 9,500 mg/kg).

DNAPL investigation at Site 88, MCB Camp Lejeune, NC

Geoprobe

Soil Cores in sample tube liners

Hot spots

Phase 2 DNAPL investigation: monitoring well installation and hydraulic testing

- Subsequent to initial core sampling, five additional cores were collected and three of these were converted to monitoring wells.
- MWs were terminated 0.5 ft into the aquitard at 18 to 20 ft below ground surface (bgs) using a 5-ft stainless steel screen.
- Upon the completion of well development,
  free-phase DNAPL was found in two of the three wells.
- From density and viscosity measurements of the collected DNAPL, it was determined that the DNAPL was almost pure PCE.

DNAPL concentrations and saturations from Phases 1 and 2

Sample ID	Depth (bgs)	PCE Conc. (mg/kg)	Organic carbon (%)	DNAPL saturation (%)*
IS10-01	15.3-15.5	48	--	0
IS10-02	16.1-16.4	16	--	0
IS10-03	17.1-17.3	19,000	--	8.26
IS10-04	17.7-17.8	2,900	--	1.11
IS12-01	15.5-15.7	37	--	0
IS12-02	16.0-16.2	20	--	0
IS12-03	17.0-17.2	25	--	0
IS12-08	16.2-16.5	--	0.36	
IS13-01	17.0-17.2	5,500	--	2.2
IS13-02	17.5-17.7	18,000	--	7.81
IS13-03	18.0-18.2	4,800	--	1.94
IS13-09	17.5-17.7	--	0.76	

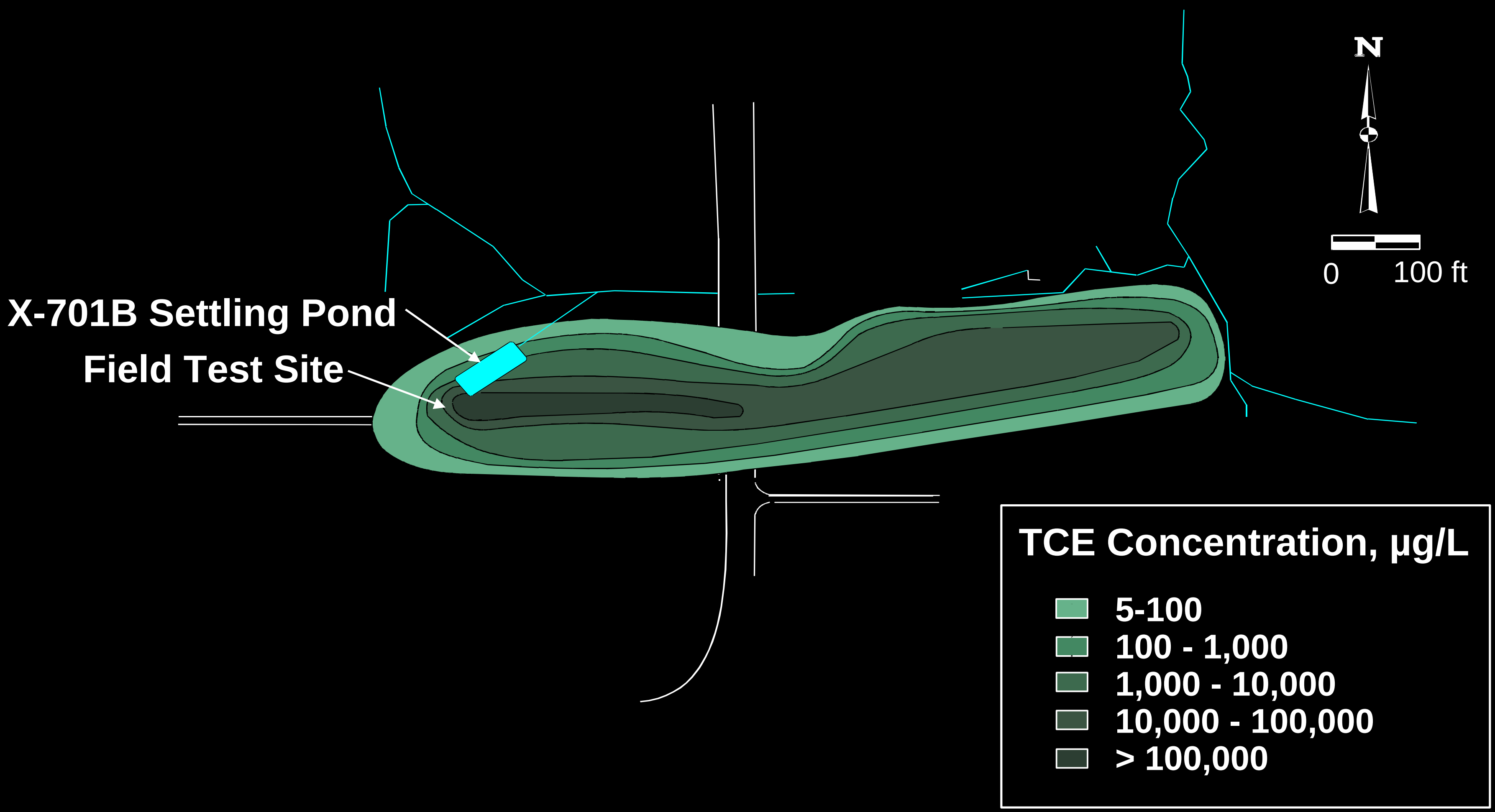
***calculated using NAPLANAL with an assumed porosity of 30% and average organic carbon of 0.58%**

Hydraulic testing at Site 88, MCB Camp Lejeune, NC

Costs of initial DNAPL investigation Site 88, MCB Camp Lejeune, NC

Soil core collection & sampling	**$ 37,288**
Geoprobe	$ 6,006
Other equipment	$ 1,245
Labor	$ 19,859
Analyses	$ 9,812
Reports	$ 366
MW install & hydraulic testing	**$ 42,633**
Drill rig	$ 9,489
Other equipment	$ 2,477
Labor	$ 16,647
Analyses	$ 6,451
Reports	$ 7,567
TOTAL	**$ 79,921**

Characterization example:
DOE Portsmouth Uranium Enrichment Plant, OH



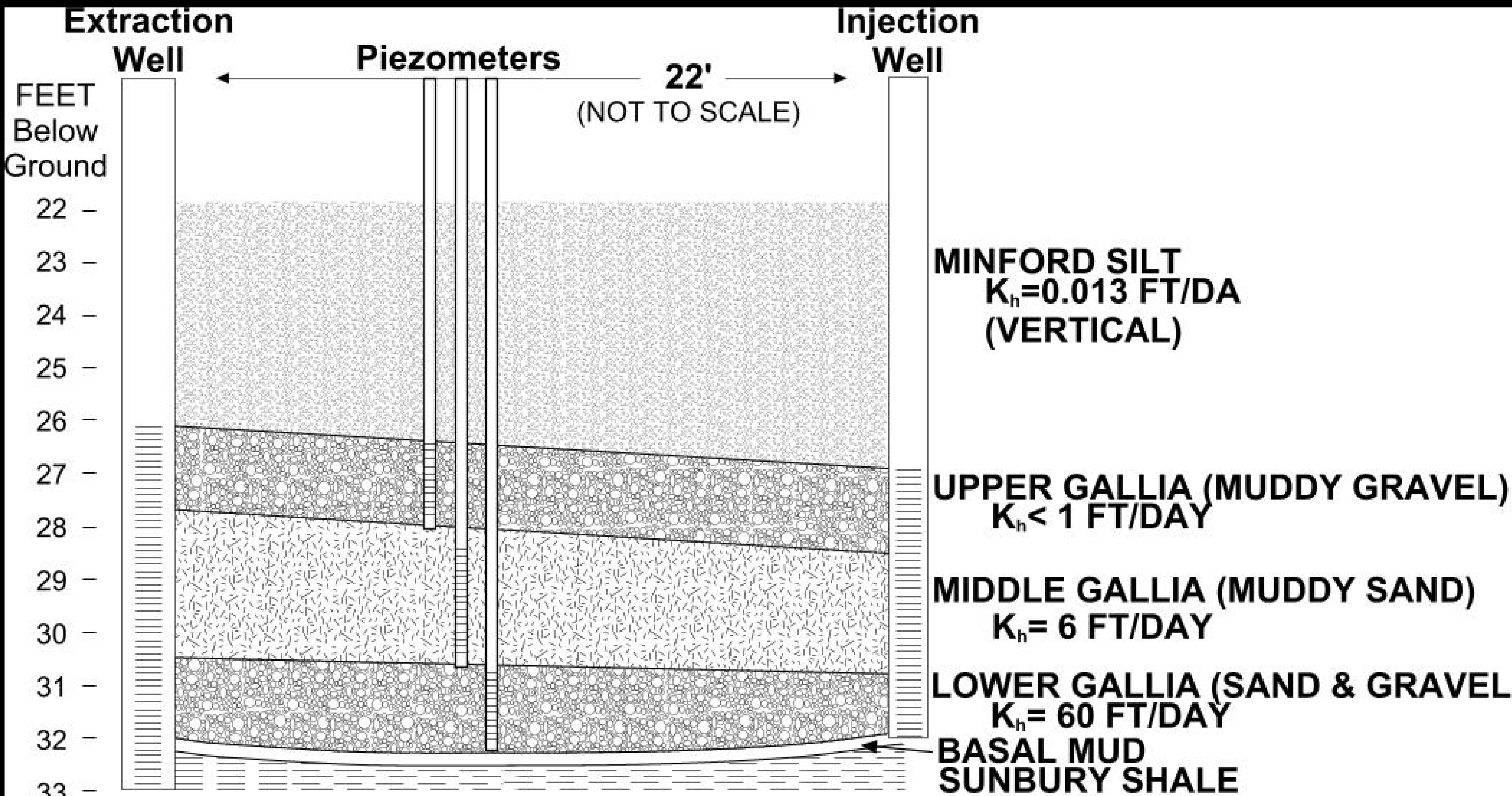
DNAPL contamination at DOE Portsmouth Uranium Enrichment Plant, OH

- X-701B settling pond received degreasing liquids
- principally TCE, some PCBs
- suspected DNAPL contamination in Gallia alluvium
- How much DNAPL is present and where is it in the alluvium?

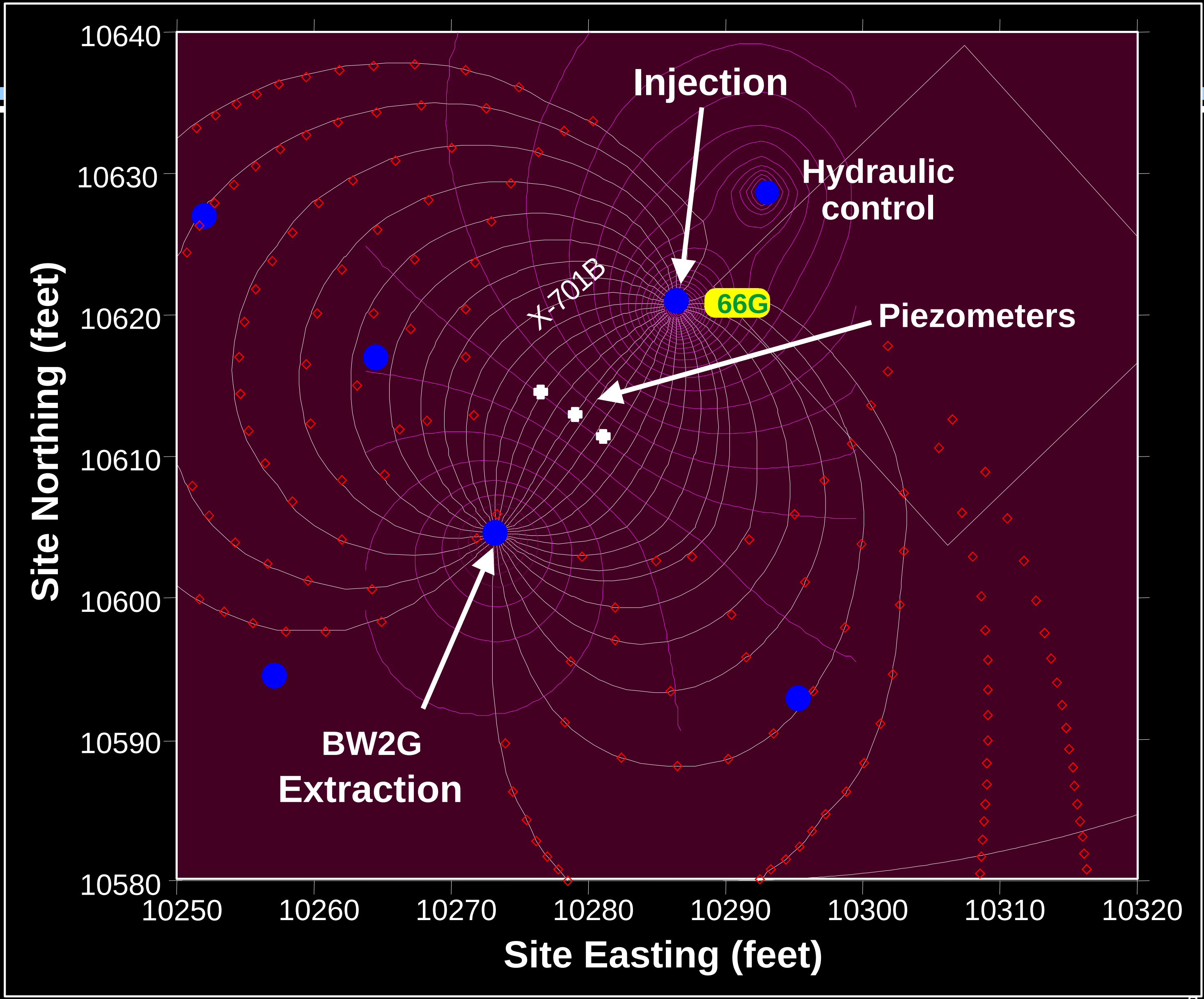
DOE Portsmouth, Approach

- conduct initial PITT to measure DNAPL and identify its spatial distribution within the Gallia alluvium;
- design and conduct surfactant test in the DNAPL-contaminated alluvia;
- conduct final PITT to assess performance of surfactant flood.

DOE Portsmouth, cross section



DOE Portsmouth, Well configuration and streamlines



DOE Portsmouth PITTs, Partition coefficients vs. TCE

Tracer	Partition coefficient
Bromide	0.0
Ethanol	0.0
Isopropanol	0.0
3-methyl-3-pentanol	4.5
hexanol	18.6
2,4-dimethyl-3-pentanol	38.2
heptanol	163
octanol	389

DOE Portsmouth PITTs: Initial and Final PITT, tracers & concentrations

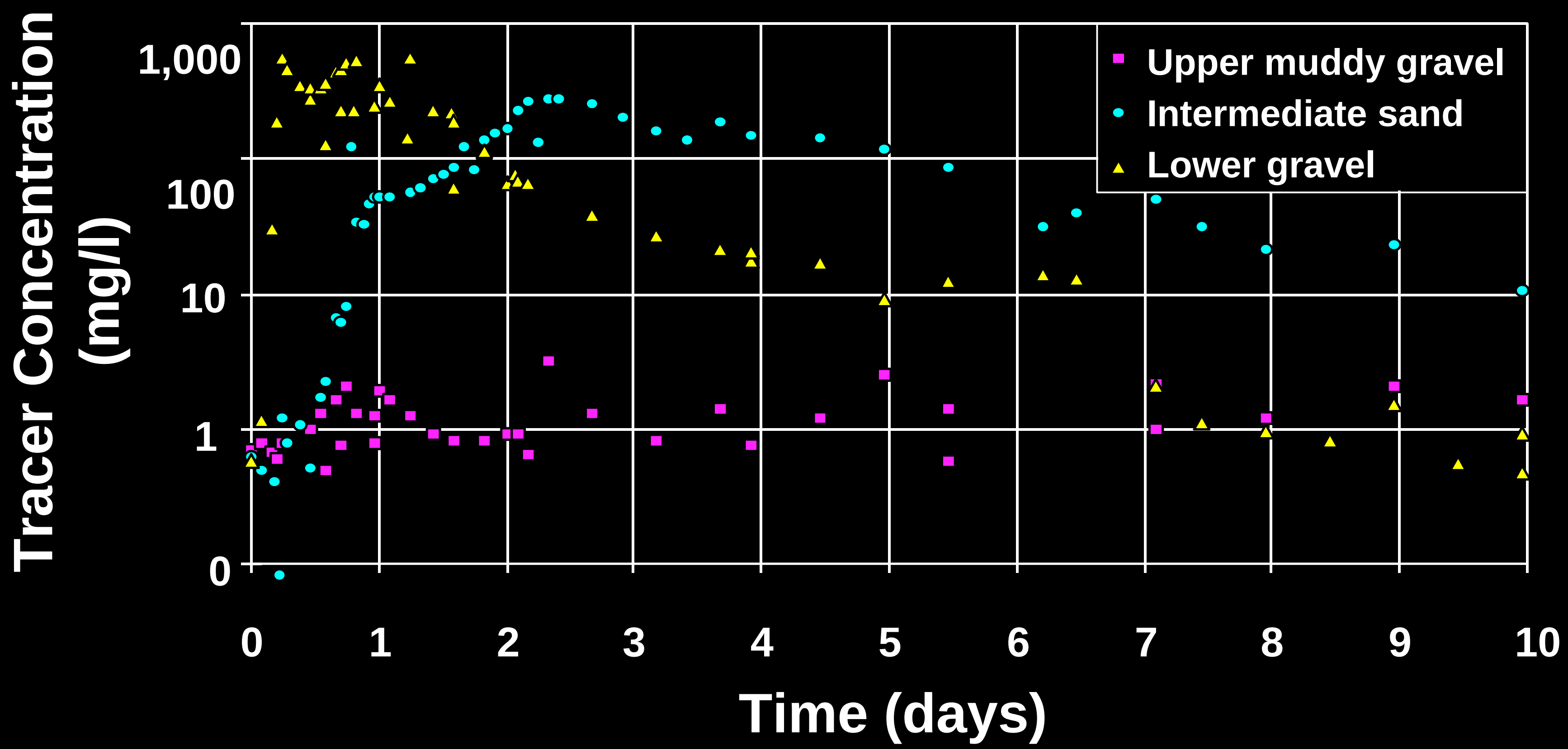
Initial PITT concentrations in mg/L

bromide	700
isopropanol	700
methyl pentanol	700
hexanol	700
dimethyl pentanol	700
heptanol	700

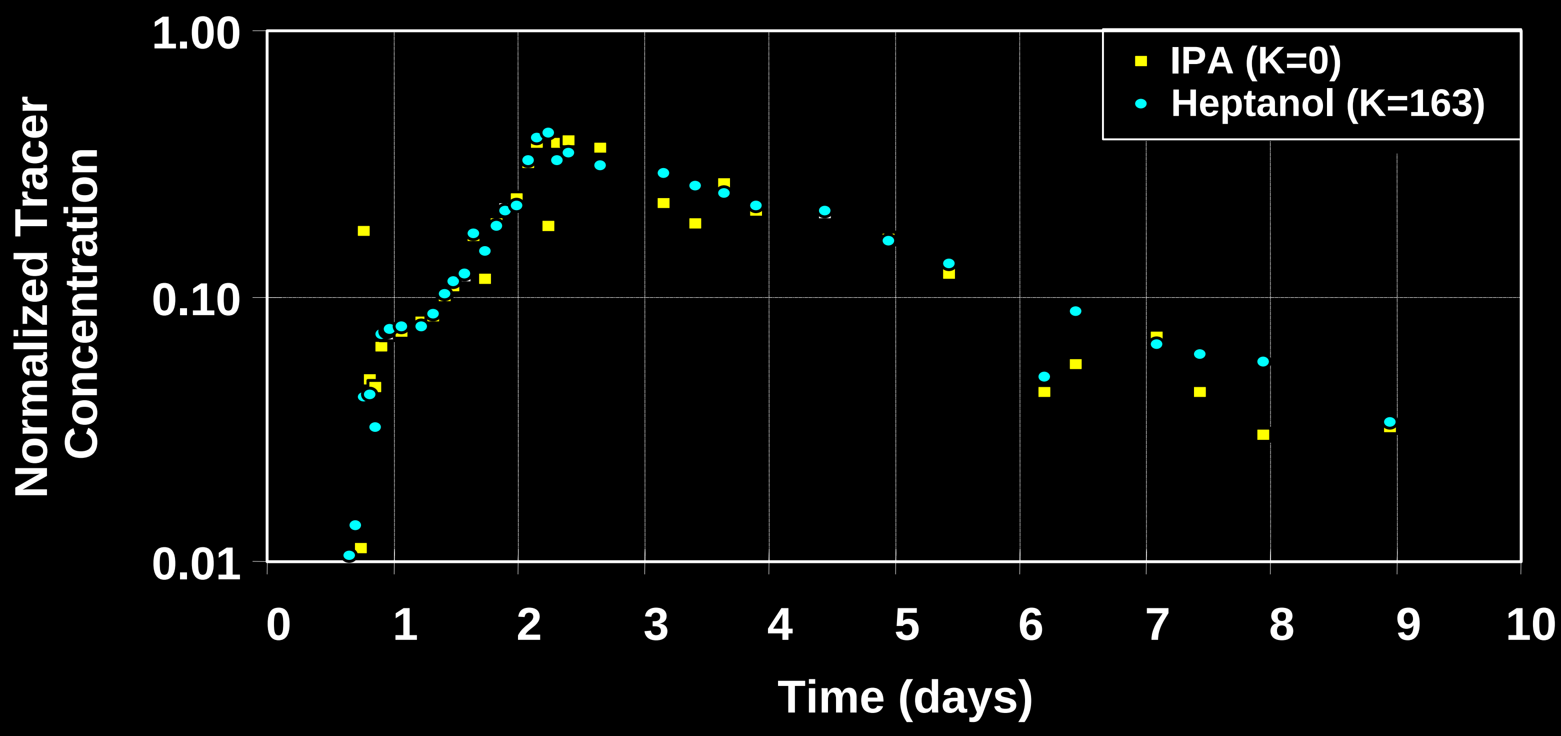
Final PITT concentrations in mg/L

bromide	700
ethanol	700
heptanol	700
octanol	200

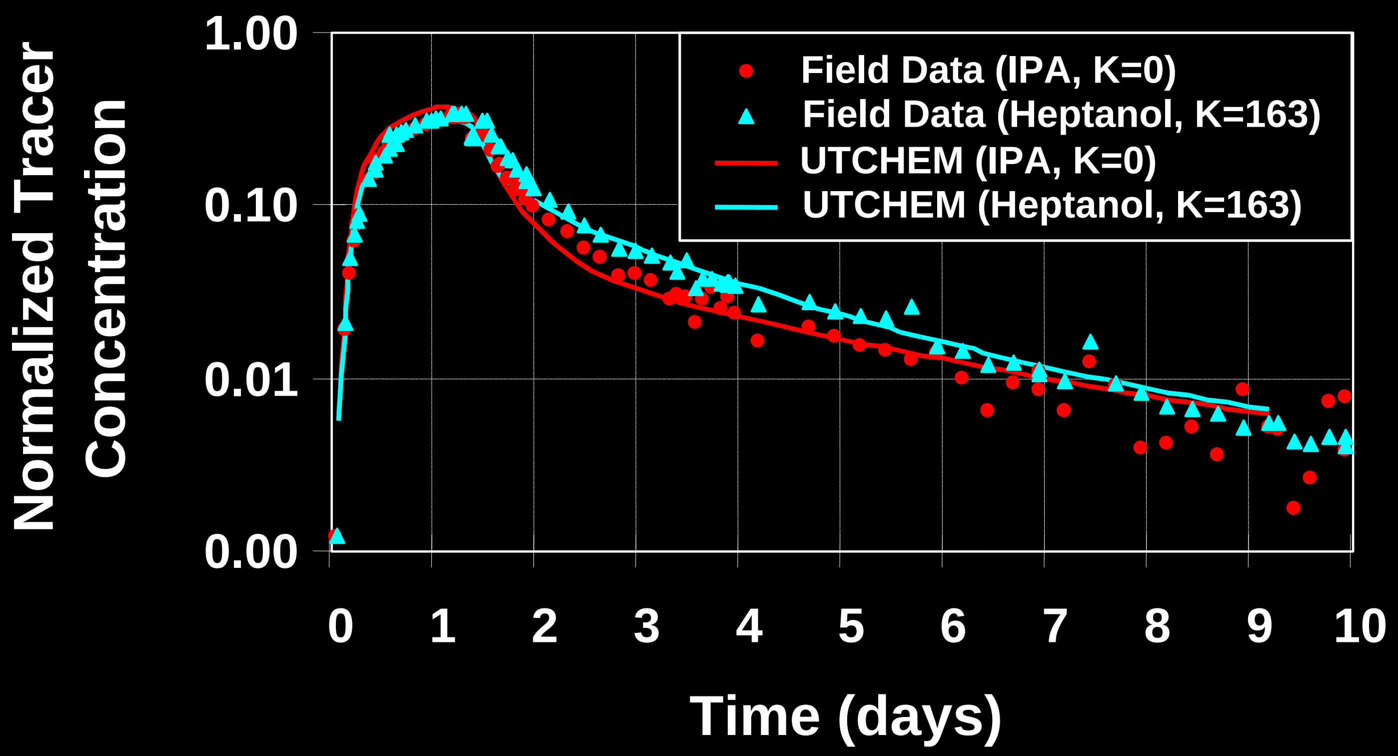
DOE Portsmouth, Initial PITT Conservative Tracer Curves



DOE Portsmouth, Initial PITT
Tracer Response Curves: Intermediate sand



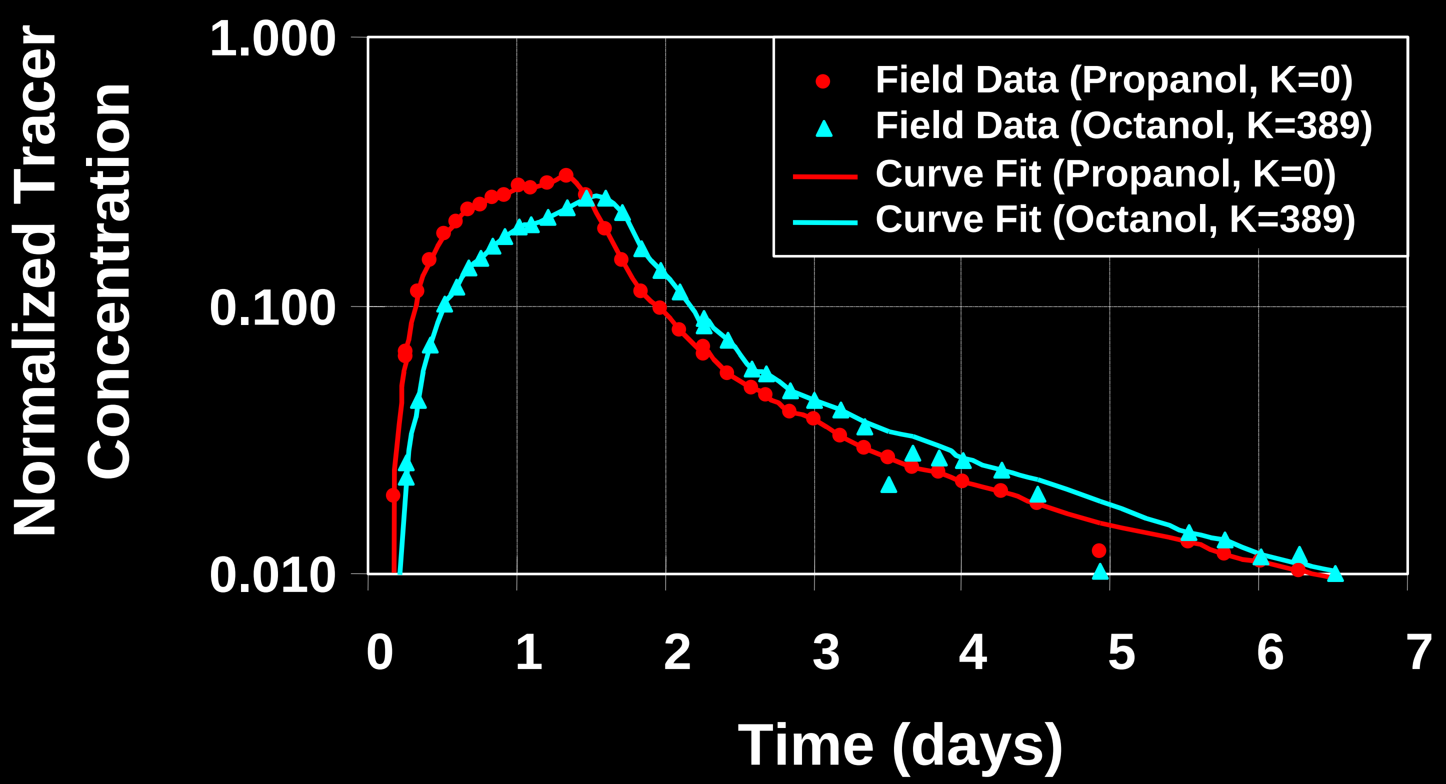
DOE Portsmouth, Initial PITT Tracer Response Curves: Lower sand & gravel



DOE Portsmouth, Results of initial PITT

- The upper muddy gravel was of such low permeability that the tracers had not entered it;
- the middle sand was clean of DNAPL;
- lower gravel contained 5-10 gals DNAPL;
- therefore DNAPL had migrated laterally into the basal gravel and not from above.
- A surfactant test and post-surfactant PITT were conducted in the lower sand & gravel zone.

DOE Portsmouth, final PITT
Tracer Response Curves: Lower sand & gravel



DOE Portsmouth,
Results of final PITT

- The final PITT indicated that approximately 2 gallons DNAPL remained in the lower sand & gravel after the surfactant test.

DOE Portsmouth PITT costs

Task	Total Cost ($)
1) Site characterization	**120K**
Soil coring and well installation	70K
Aquifer testing and analyses	50K
2) Tracer selection and test design	**90K**
Tracer selection	40K
Test design	50K
3) Field demonstration	**110K**
Fieldwork	90K
($5K chemicals, $20K equipment, $65K labor)	
Analyses	20K
4) Final report	**40K**
TOTAL	**360K***

***With the second PITT, the per PITT costs reduce to $235K**